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Chapter 5: Potential Impact of Ethanol-containing Gasoline on Surface Water Resources

Authors

David Layton*
Jeffrey Daniels*

Editor
G. Cannon*

Contributor

B. Clark*

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Lawrence Livermore National Laboratory, Livermore, CA 94550

University of California • Livermore, CA 94550
Lawrence Livermore National Laboratory
Environmental Restoration Division

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5. Potential Impact of Ethanol-containing Gasoline on Surface-water Resources

5.1. Introduction

The phaseout of methyl tertiary butyl ether (MTBE) from gasoline in California will result in changes in the composition of gasoline in order to meet air-quality requirements. For example, unless a Clean Air Act requirement for oxygen content is waived for California, ethanol will have to be added to gasoline sold in areas that have not attained compliance with air-quality standards for ozone. The importation, distribution, and use of large quantities of ethanol in the state raises potential concerns regarding impacts to surface-water supplies from accidental releases, discharges from recreational boats, and washout of ethanol from the atmosphere. In this assessment, we review information on the environmental chemistry of ethanol and conduct a series of screening-level simulations of various releases in order to understand the nature and magnitude of potential impacts to surface waters. To put the results in perspective, we compare the environmental behavior of ethanol with that of MTBE.

5.2. Background

Ethanol (EtOH) and MTBE are fuel compounds that have been added to gasoline for many years. These compounds contain elevated amounts of oxygen (that is, 18 and 35 wt% for MTBE and ethanol, respectively), and they have octane numbers over 100. In Table 5-1 we summarize some of their key physicochemical properties affecting their behavior in the environment. Both EtOH and MTBE are hydrophilic substances, with low octanol-water partition coefficients and elevated solubilities in water (ethanol is miscible in water, and MTBE has a solubility of 488 mol/m^3, or 43 g/L). Ethanol is subject to fairly rapid biodegradation in the hydrosphere, but MTBE is recalcitrant biologically. Reviews of the environmental chemistry of these oxygenated fuel compounds are contained in the *Interagency Assessment of Oxygenated Fuels* (National Science and Technology Council [NSTC], 1997), and in reports by Malcolm Pirnie, Inc. (1998a,b).

5.3. Washout of Ethanol and MTBE from the Atmosphere

Both ethanol and MTBE can enter the atmosphere directly as a consequence of volatilization during different stages of their life cycles, such as fugitive or accidental emissions from manufacturing, distribution, and use, and from incomplete combustion. Although these volatilized compounds may undergo some degree of degradation in the atmosphere, that fraction that is not degraded by chemical processes will be subject to washout by precipitation. Accordingly, any significant rainout (i.e., wet deposition) can potentially impact surface waters. To determine the significance of rainout, we estimated the concentrations of MTBE and ethanol in rainwater during a precipitation event based on atmospheric concentrations of 1 part per

billion by volume (ppb[v]) or for any other concentration of a substance (s) in units of ppb(v), (that is, 10^{-9} L_s/L_{air}) using Equation (5-1)

$$C_{rain} = \frac{C_{air}\, M_s\, cf\, P}{H'\, R\, T},$$

(5-1)

where

    C_{rain} = concentration of substance in rain, $\mu g/L$;

    C_{air} = concentration of substance (s) in air, ppb(v);

    M_s = molar mass (molecular weight) of substance (s), g/mol;

    P = pressure, 1 atm;

    R = gas constant, 0.0821 atm-L/mol-K;

    T = temperature, K;

    cf   = conversion factor, 10^6 $\mu g/g$; and

    H' = dimensionless Henry's law constant (that is, C_{air}/C_{water}).

An important property with respect to rainout is the dimensionless Henry's law constant, which essentially describes the propensity for a compound to volatilize to air from water, or conversely, to enter water and remain in the water phase. The dimensionless Henry's law constant (H') is expressed mathematically as the ratio of the air-to-water concentrations of a compound at equilibrium (Zogorski *et al.*, 1997). Ideally, when an ambient air concentration for a substance is multiplied by $1/H'$, the result is the concentration in the rainwater phase. The ratio of the dimensionless Henry's law constants for a temperature of 298 K for MTBE and ethanol, respectively, exceeds a factor of 80 (H' for MTBE = 2.16×10^{-2}, and H' for ethanol = 2.57×10^{-4}). Therefore, based on H' alone, more ethanol than MTBE will be present in rainwater during a precipitation event, especially if both are present at equal concentrations (expressed as mass per unit-volume [for example, $\mu g/L_{air}$]).

As expected, applying Equation (5-1) reveals that the estimated concentration of ethanol in rainwater for a 1-ppb(v) concentration of ethanol in air (that is, 1.9×10^{-3} $\mu g/L$ or 41 n mol/ m^3) could be as high as 7.3 $\mu g/L$ (160 n mol/L) during a precipitation event; whereas, a 1-ppb(v) concentration of MTBE in air (that is, 3.6×10^{-3} $\mu g/L$ or 41 n mol/ m^3) would yield only about 0.17 $\mu g/L$ (1.9 n mol/L) in rainwater during a precipitation event. This difference of more than a factor of 40 in mass per unit-volume rainwater concentration (almost two orders of magnitude in moles per unit volume) is due to the large difference between the dimensionless Henry's law constants for the two compounds because the mass per unit-volume atmospheric concentration for MTBE is only about a factor of two greater than that for ethanol.

Equation (5-1) is particularly useful when considering the atmospheric levels of MTBE and ethanol in a specific air basin, such as the greater Los Angeles region of California. For

example, Allen *et al.* (1999a) have estimated emissions and annual-average air concentrations for MTBE and ethanol for 1997 and 2003 in the greater Los Angeles air basin. According to that data, the emissions of MTBE could decline by 32% between 1997 and 2003. Corresponding maximum, annual-average atmospheric concentrations in the greater Los Angeles air basin[1] are 3.9 and 2.6 ppb(v) (160 and 100 n mol/ m^3, respectively). From Equation (5–1), it is estimated these concentrations could yield maximum, average concentrations of MTBE in rainwater during a precipitation event of 0.65 and 0.43 µg/L (7.4 and 4.9 n mol/L, respectively). Similarly, the assessment performed by Allen *et al.* (1999a,b) suggests vehicular emissions of ethanol in the air basin could increase ambient levels of ethanol by as much as 50% (from a value of 5.1 ppb[v] [210 n mol/m^3]) to a value of 7.6 ppb[v] [300 n mol/m^3]) if ethanol is added to gasoline in 2003 to achieve 2 wt% oxygen; or ambient concentrations of ethanol could rise more than 72% (from 5.1 ppb[v] [210 n mol/m^3] to 8.8 ppb[v] [370 n mol/m^3]) if ethanol is added to gasoline in 2003 to achieve 3.5 wt% oxygen. According to Equation (5–1), the corresponding concentrations of ethanol in rainwater for ambient levels of 5.1, 7.6, and 8.8 ppb(v) (210, 300, and 370 n mol/m^3) would be 37, 56, and 64 µg/L (about 800, 1200, and 1400 n mol/L, respectively).

5.4.   Releases to Rivers and Streams

We employed a two-tiered approach for evaluating the potential water-quality impacts on rivers and streams caused by releases of ethanol. First, we examined the relative effectiveness of volatilization and biodegradation as removal mechanisms, using a modified version of a methodology presented by Pankow *et al.* (1996). We then analyzed the consequences of a major release to a river using a surface-water transport model. Based on the results of these analyses, we identified uncertainties and data gaps that need to be addressed to improve our ability to predict the behavior of ethanol in aquatic environments.

5.4.1. Volatilization and Biodegradation of Ethanol in Rivers and Streams

Pankow *et al.* (1996) presented a methodology for calculating the volatilization rates of fuel-oxygenate compounds in rivers and streams. In their methodology, the half-life of a compound is calculated using a rate constant for volatilization calculated from its mass-transfer velocity (from the water column to air) and the depth of the river. Losses due to transformation processes, such as biodegradation, were not considered. However, if such transformation processes are rapid, they can be as effective as volatilization losses in reducing the concentrations of the fuel compounds dissolved in water. We, therefore, calculated the half-life of a fuel oxygenate due to the combined processes of volatilization and biotransformation as

$$t_{half} = \frac{0.693}{\left(k_v + k_b\right)}, \tag{5-2}$$

where

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[1] As indicated by either the "best" or "upper" baseline, population-weighted annual exposure for summer, which is probably a lower value than that for winter, according to Allen *et al.* (1999b).

t_{half} = half-life of oxygenate in surface water, d;

k_v = rate constant for volatilization, 1/d; and

k_b = rate constant for biodegradation, 1/d.

Pankow *et al.* (1996) also introduced another measure of the persistence of a compound, termed the "half-life distance," which is simply the distance traveled during the half-life of a compound,

$$d_{half} = u_w t_{half}, \tag{5-3}$$

where u_w is the velocity of the water (m/d).

As a means of evaluating the various parameters that control the persistence of ethanol released to a river, we examined two transport cases (after Pankow *et al.* [1996]), one for conditions supporting reduced volatilization (that is, calm winds at 0.25 m/s, a river-flow velocity of 2732 m/d, and a river depth of 3 m) and enhanced volatilization (that is, high winds at 5.5 m/s, a river-flow velocity of 27,320 m/d, and a river depth of 1 m). With a water temperature of 25°C, the volatilization-rate constants (that is, k_v) for ethanol are 0.017/d for the conditions associated with reduced transfer to atmosphere and 0.21/d for enhanced conditions (equivalent half-lives of 40 and 3.3 days with half-life distances over 90 km). In contrast, the rate constants for MTBE determined using the same conditions are significantly higher—0.083/d and 1.3/d (with correspondingly lower half-lives of 8.4 and 0.52 days and associated distances of 23 and 14 km) for reduced and enhanced volatilization, respectively. Ethanol has a much lower Henry's law constant than MTBE; and consequently, the relative importance of the air-side mass-transfer velocity in controlling the overall mass transfer to air is more important (see Appendix A).

The persistence of ethanol in surface water, however, is also a function of its biodegradation rate. As already explained (see Alvarez and Hunt, 1999, Vol. 4, Chapter 3 of this report), ethanol represents a carbon and energy source for microorganisms[2]. Howard *et al.* (1991) comment that, according to best scientific judgment, the aerobic-biodegradation half-life of ethanol in surface water is estimated to range from 6.5 h to 26 h. This judgment is consistent with results from an experiment performed by Apoteker and Thévenot (1983) to study the biodegradation of ethanol in samples of Seine river water that were incubated at 20°C. This experiment produced an exponential-growth-phase rate constant of 0.22 per hour, from which the aerobic-biodegradation half-life can be estimated to be about 3.2 h (that is, 3.2 h = 0.693/[0.22 per h]). However, this exponential growth-phase was preceded by a 10-h lag phase, and so the effective half-life for ethanol is closer to 13 h, rather than 3 h. This biphasic behavior was interpreted by Apoteker and Thévenot (1983) to occur as a result of microorganism adaptation to a change in environment, which involved the sudden introduction of the new substrate compound (that is, ethanol). Both the lag time and subsequent degradation rate are expected to vary by receiving-water body properties as discussed by Alvarez and Hunt (1999, Vol. 4, Chapter 3 of this report). With a biodegradation half-life of 13 h, the rate constant for EtOH becomes 1.3/d, which is comparable to the volatilization rate constant for MTBE under enhanced transport conditions.

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[2] In comparison to ethanol and most other gasoline components, MTBE is considered resistant to aerobic microbial degradation (Suflita and Mormile, 1993).

Biodegradation is particularly sensitive to temperature, decreasing with decreasing temperature. This low-temperature effect occurs because low temperatures reduce cellular membrane fluidity and permeability, which thereby reduces the uptake of both nutrients and contaminants. Thomann and Mueller (1987) suggest that the biodegradation rate for temperatures other than 20°C can be adjusted using the following relationship:

$$k_{b(T)} = k_{b(20)} 1.06^{(T-20)},$$
(5-4)

where T is in degrees centigrade. Thus, if the water temperature were 5°C, the resulting biodegradation rate would only be about 40% of the rate at 20°C. Temperatures warmer than 20°C increase the rate of biodegradation by improving enzymatic activity up to an optimum value that is specific to the microbial species (see Alvarez and Hunt, 1999, Vol. 4, Chapter 3 of this report). At temperatures above the species-specific optimum, proteins and nucleic acids become denatured and inactive; and the biodegradation process will cease. Given the variable effects of temperature and the microbial characteristics of different receiving waters, a nominal half-life for ethanol of 24 h can be assumed.

5.4.2. Accidental Releases of Ethanol to Rivers and Streams

The transport of ethanol to various locations in California where it would be blended with gasoline raises the possibility that transportation accidents could occur that impact rivers and streams. There are potentially many different scenarios that could be constructed to assess the consequences of such accidents. We note, however, that the transport of ethanol is not inherently any different than the transport of other bulk liquids; hence, the likelihood of releases should not differ either. For the purposes of this screening-level assessment, therefore, we simply postulated an accidental release in which a rail tank car carrying 30,000 gal of ethanol derails and discharges its entire inventory to a river. To estimate the concentrations of ethanol in water resulting from such a hypothetical release, we have adopted an empirically-based methodology developed by Jobson (1996) that is especially suited for cases where there are limited amounts of hydrologic information on an impacted river.

The basic equation for determining the peak downstream concentration of a substance spilled into a river is:

$$C_{pc}(T_{pc}) = \frac{k_{pc}(T_{pc}) M_s e^{-k_{tot} T_{pc}}}{\text{nf } Q}$$
(5-5)

where,

$$T_{pc} = \frac{x}{V_{pc}}$$
(5-6)

and

$C_{pc}(T_{pc})$ = peak concentration (*pc*) of spilled contaminant at a given downriver location at time T_{pc}, mg/L;

k_{pc} = dissipation-rate constant of the peak concentration (*pc*) due to longitudinal dispersion, 1/s;

T_{pc} = arrival time of the peak concentration (*pc*) at a location downstream of the release point, h;

x = distance to receptor location downstream of spill site, m;

v_{pc} = velocity of the peak concentration (*pc*) of the plume, m/s;

M_s = initial mass of the substance (*s*) discharged, mg;

k_{tot} = loss-rate constant for volatilization and degradation, 1/d (note: for ethanol there is minimal degradation);

nf = normalization factor introduced by Jobson[3] (1996), 1×10^6 (dimensionless); and

Q = volumetric-discharge rate for the river at time of release, L/s.

   The time-concentration profile of a contaminant at a fixed location downstream from a spill site is a complex function of channel properties, flow rate, drainage, slope, etc. As a water-borne plume of spilled material is transported downstream, the plume will spread longitudinally in the direction of river flow, creating a gaussian-type pattern of contaminant concentrations in the river at any given point measured downstream (Hemond and Fechner, 1994). Longitudinal dispersion increases with the travel time of the plume, causing the peak concentration to decrease as the plume-width spreads. Jobson (1996) developed an empirical relationship that estimates the value of the rate constant describing the reduction of the peak concentration (that is, k_{pc}) in terms of plume travel time, and the ratio of the volumetric-discharge rate at the time of the release to the mean-annual volumetric-discharge rate of the stream (see Appendix B).

   As described in Equation 5-6, the travel time of the plume's peak concentration is equal to the distance from the release point to the downstream receptor location divided by the velocity of the plume's peak concentration in the river. Jobson (1996) developed a set of empirical relationships to determine the velocity of the peak concentration in the dispersing plume, as well as its maximum probable velocity (see Appendix B). Input parameters include the drainage area of the watershed, the slope of the river channel that the plume is transiting, the volumetric-discharge rate at the time of release, and the mean annual volumetric-discharge rate of the river at a receptor location. To assess the consequences of the postulated spill, we used the hydrological parameters of the Sacramento River (in California), south of Dunsmuir and north of Lake Shasta. This particular section of the river has a railroad line adjacent to it and was impacted by a tank car spill in 1991 (California Central Valley Regional Water Quality Control Board [CalCVRWQCB], 1991). The associated watershed has a drainage area of 1100 km^2 (425 mi^2), a slope of 0.015, an average annual-average volumetric-discharge rate of 32.1 m^3/s

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[3] The factor 10^6 arises from the fact that Jobson (1996) defines a "unit concentration" (identified as k_{pc} in Equation [5-5]) as 10^6 times the concentration produced in a unit discharge due to the injection of a unit mass of substance. Jobson (1996) relates the "unit concentration" to a mass flux of solute (mass/time) per unit of mass injected.

(1133 ft^3/s) (see U.S. Geological Survey [USGS], 1999). The assumed volumetric-discharge rate at the time of the hypothetical release is 5.6 m^3/s (200 ft^3/s).

The best estimate for the velocity of the peak concentration of the dispersing plume is 1.2 km/h, while the maximum probable velocity is 2.1 km/h, or almost double the best estimate (see Appendix B). A biodegradation half-life of 24 h was used to simulate the *total* loss rate of ethanol (volatilization loss is minimal for ethanol). Figures 5-1 and 5-2 depict the decreases in the peak concentrations as a function of distance downriver from an assumed release point. The predicted concentrations are highest for the maximum probable velocity of the peak concentration for the dispersing plume, because at high velocity less longitudinal dispersion occurs within the plume during transit over a given distance. Under the spill scenario considered here, the concentrations in river water could affect aquatic species. In a review of the aquatic toxicity of ethanol, for example, Malcolm Pirnie, Inc., (1998a) reported that the LC$_{50}$ (lethal concentration for 50% of a population) for different aquatic species ranged from 454 to 14,740 mg/L. The toxic levels of ethanol would, therefore, be expected to occur at variable distances downstream from the hypothesized spill, with the extent of such toxic concentrations depending on volumetric-discharge conditions. As shown in Figures 5–1 and 5–2, toxic effects could occur many kilometers downstream for a catastrophic release, such as the one that was simulated. For example, if the average volumetric-discharge rate (that is, 32.1 m^3/s) were selected at the time of release, instead of the low volumetric-discharge rate we chose to use, the predicted concentrations would be nearly a factor of six lower—reducing the extent of any possible toxic effects to aquatic species. In addition, if only a portion of the tank-car inventory were released, the resulting concentrations would also be reduced proportionately. Aside from the acute toxicity for aquatic species that might be associated with a spill and their associated recovery, it is unlikely that there would be any long-term toxic effects, as the ethanol will not persist in water because of its rapid biodegradation.

5.5   Releases to Reservoirs and Lakes

One of the unexpected surface-water impacts resulting from the use of MTBE in reformulated gasoline is the occurrence of MTBE in reservoirs and lakes in California (see McCord and Schladow, 1998; Malcolm Pirnie, Inc., 1998b). The principal source of this contamination is recreational boating (Reuter *et al.*, 1998), particularly carbureted two-stroke engines (see Appendix C). Consequently, such recreational watercraft could also represent a potential source of ethanol in surface waters used for boating. In order to assess the significance of ethanol discharges from watercraft to surface waters, we have conducted a screening-level analysis in which we compare the water-quality impacts of MTBE discharges into a lake with those associated with ethanol.

5.5.1. Background: Watercraft Releases of Fuel Compounds

Concerns over the impacts of motorized watercraft on the quality of Lake Tahoe prompted the Tahoe Regional Planning Agency to invoke a ban on two-stroke marine engines. The ban was effective on June 1, 1999; and consequently, this provided a unique opportunity to investigate the differences in the concentrations of MTBE and other fuel compounds in lake water before and after the ban. Appendix C contains the results of a study recently completed by

Allen and Reuter of the Tahoe Research Group at the University of California at Davis, California. This study tracks the changes in fuel compounds in Lake Tahoe from 1997–1998 to 1999. They found that there were significant decreases in the concentrations of MTBE and benzene, toluene, ethyl benzene, and xylene (BTEX) compounds after the ban. For example, for 1999 the mean concentrations of MTBE and toluene were 95.8 and 88.3% lower, respectively, than the levels reported in 1997–1998. The only exception in 1999 was that isolated activities associated boat launch areas, marinas, etc., produced elevated levels in certain locations or "hot spots."

5.5.2. Water Quality Impacts of MTBE and Ethanol Due to Recreational Boating

The concentrations of fuel hydrocarbons in recreational lakes or reservoirs are a function of the types of watercraft operated (that is, the mix of two-stroke versus four-stroke engines), the temporal pattern of recreational boating (particularly during the summer months and peak vacation periods), and the limnology of the surface water. Important limnologic parameters determining the magnitude and persistence of fuel compounds discharged into water are the mixing or dilution volume of surface water, wind velocity, water temperature, and rate of water flowing through the mixing volume. The primary determinant of the mixing volume is the depth of the epilimnion, or the relatively warm layer of water that sits atop the colder, denser waters of the hypolimnion. Volatilization of fuel compounds increases as the wind velocity rises, thereby decreasing the depth of the surface-boundary layer (which, in turn, increases the mass-transfer velocity of dissolved fuel compounds). Water temperature influences the rates of volatilization and biodegradation. The flow of water through the epilimnion is another mechanism for reducing residual levels of dissolved fuel compounds.

During the summer boating season, the peak discharges of fuel compounds and their related concentrations in water coincide with the holidays (namely, Memorial Day, Fourth of July, and Labor Day), when boating activity increases (Reuter *et al.*, 1998). Needless to say, it is not possible to simulate the levels of fuel compounds in water at a given lake unless watercraft usage is known along with fuel-discharge rates to water. However, as a screening-level analysis, we have chosen to simulate a discrete period of watercraft discharges at Donner Lake in northern California, using data presented in studies by McCord and Schladow (1998) and Reuter *et al.* (1998).

The total mass and concentration of a fuel compound in the epilimnion after a continuous watercraft discharge of a fixed duration can be estimated from

$$M_{s,ep}(T_d, t) = \frac{E_r \, \mathrm{cf}}{k_{tot}} \left[1 - e^{-k_{tot}T_d} \right] e^{-k_{tot}t} \tag{5-7}$$

and

$$C_{s,ep} = \frac{M_{s,ep}(T_d, t)}{V_{ep}}, \tag{5-8}$$

where

$M_{s,ep}(T_d,t)$ =   mass of substance (i.e., fuel compound, s) in the epilimnion (ep) at time t (days) after a continuous discharge of duration T_d (days), µg;

$C_{s,ep}$ =   concentration of the substance (i.e., fuel compound, s) in the epilimnion (ep), µg/L;

E_r =   constant discharge rate of substance (i.e., fuel compound, s) from boating activity, *kg/d*;

cf   =   conversion factor, 10^9 µg/kg;

k_{tot} =   first-order loss rate for volatilization and biodegradation, 1/d; and

V_{ep} =   volume of the epilimnion (ep), L

Reuter *et al.* (1998) reported that during a seven-day period lasting from July 1–7, 1997, the total mass of MTBE in Donner Lake rose by 250 kg, resulting in an increase of 10 µg/L in the epilimnion of the lake. The depth of the epilimnion by July was between 9 and 11 m, and the average daily wind velocities from March to November 1997, ranged from 1.7 to 2.1 m/s. After the last major boating activity associated with Labor Day, the mass of MTBE dropped at a rate of 8.1 kg/d, which, according to Reuter *et al.* (1998), reflects a half-life of 14 days (equivalent to a first-order loss rate of 0.05/d). The MTBE loss rate was smaller after the July 7th peak (that is, 6.7 kg/day); however, inputs of MTBE from watercraft still occurred, so that this loss rate is not an accurate indicator of volatilization losses.

We can estimate the average discharge of MTBE into the lake during this seven-day period by solving for E_r in Equation (5-7) and setting $M_{ep}(T_s,t)$ = 250 kg, k_{tot} = 0.05/d, T_s = 7 days, and t = 0 day. The resulting discharge rate is 42 kg/d. As an alternative, we also calculated the value of k_v ($\cong k_{tot}$, because MTBE's biodegradation is assumed to be negligible) for MTBE using the mass-transfer velocities estimated from the physicochemical properties of MTBE, wind speed, and mixing depth (as presented in the Appendix A). We used the temperature-dependent equation for estimating H_L given in Robbins *et al.* (1993) to estimate a value of 43 Pa-m^3/mol for MTBE at 20°C. Loss-rate constants were computed for alternative values of the depth of the epilimnion and wind velocities for the seven-day period in July and are shown in Table 5-2. McCord and Schladow (1998) indicate that the average wind speed was approximately 3 m/s and the surface area of the lake was 3.6 km^2. While the depth of the epilimnion across the lake was about 10 m, the effective transport depth for MTBE was probably smaller, based on the portions of lake-surface area overlying regions with water depths under 10 m. Accordingly, we have provided in Table 5-2 estimates of the loss-rate constants for varying depths of the epilimnion and also two different wind speeds. We also show the corresponding mass loadings and concentrations of MTBE in the epilimnion at the end of a seven-day period during which time total MTBE discharged to the lake was considered to be at a constant rate of 40 kg/d from watercraft.

The predicted concentrations decrease with increasing depth of the epilimnion because the mixing volume increases, reducing the concentration of MTBE. The predicted mass loadings increase due to the reduction in loss rates caused by smaller mass-transfer rates as the depth of

the epilimnion increases. The best agreement with the observed MTBE loadings and concentrations is for an epilimnion layer of 7 m and a wind speed of 2 m/s. However, all of the predicted values are in general agreement with the values reported by Reuter *et al.* (1998)—given the uncertainties in both the measurements (for example, sampling biases) and the mass-transfer models.

We used the MTBE-release case for Donner Lake as the basis for assessing the nature and magnitude of surface-water quality impacts of ethanol discharged from watercraft. The reference epilimnetic depth of the lake was set at 8 m and the wind speed is 3 m/s. We used the Henry's law constant given at 25°C (see Table 5–1) to estimate volatilization losses (which are negligible for ethanol). To bracket the range of potential biodegradation losses, we estimated concentrations for biodegradation half-lives of 12, 24, and 48 h. In Figure 5-3, we show the predicted concentrations of ethanol in the lake's epilimnion after a continuous discharge of 40 kg/day of ethanol lasting seven days. With a nominal biodegradation half-life of 24 h, the peak concentration is 2 µg/L, compared with 8.3 µg/L for MTBE with the same source term (Table 5-2).

5.6.　Summary

A quantitative risk assessment designed to compare the results of MTBE and ethanol releases to surface waters was not performed and was not the objective of this chapter. Instead, we performed a series of screening-level simulations of various releases to better understand the nature and magnitude of the impacts of ethanol and MTBE on surface waters both temporally and spatially. However, based on the health-protective concentrations for drinking water alone, (which are summarized by the State of California Environmental Protection Agency, Office of Environmental Health Hazard Assessment in Volume 5 of this report [CalEPA/OEHHA, 1999]), it is clear that any catastrophic or even major release of MTBE to surface water is far more likely to represent a potential public-health problem than a similar release of ethanol. This is because the draft health-protective concentration for oral exposures to drinking water for ethanol is 1,100,000 µg/L, whereas the public-health goal for drinking water for MTBE is only 13 µg/L—a difference of almost 5 orders of magnitude (that is, 10^5 or 100,000). The problem of MTBE release to surface water is further exacerbated because it appears to be recalcitrant to aerobic biodegradation (Suflita and Mormile, 1993).

Our analyses indicate that ethanol is considerably less volatile than MTBE in surface waters because of its low Henry's law constant. Although its volatilization-loss rate from water will be much less than that of MTBE, it will not persist in water because it undergoes fairly rapid biodegradation.

The primary uncertainties associated with ethanol in surface water are associated with the determination of biodegradation rates for specific surface waters, including lakes and streams, as a function of water temperature, oxygen content, etc. Also, temperature-dependent values for the Henry's law constant would improve estimates of air/water partitioning for different ambient conditions.

A key data gap involves the potential impact that rainout will have on surface waters situated in urban areas where the ambient concentrations of ethanol are predicted to be the highest.

Ethanol in urban runoff will undergo biodegradation in surface waters; however, there will be a balance between the inputs from rainfall and losses due to degradation—with the sequencing between storms an important variable in determining the average concentrations in surface-water supplies.

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Figures
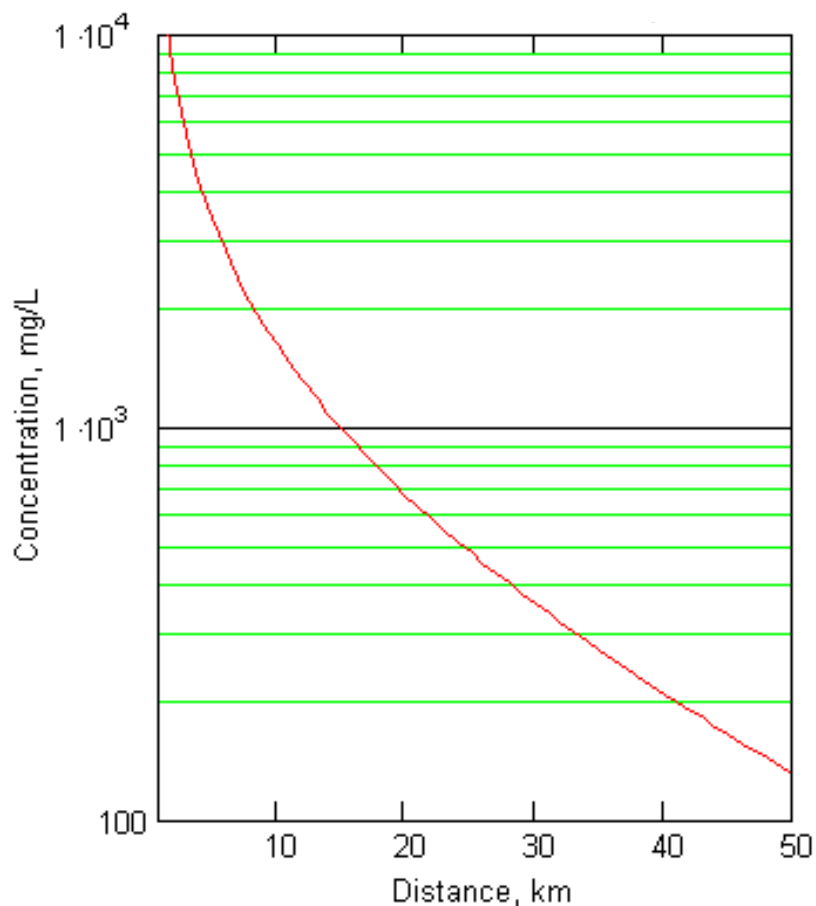
Figure 5-1. Peak concentrations of ethanol in a channel of the Sacramento River above Lake Shasta after a hypothetical tank-car release. Concentrations are based on an estimate of the most likely river-flow velocity for peak concentration (see Appendix B) and a biodegradation half-life of 24 h for ethanol (representing k_{tot} in Equation [5-5]).
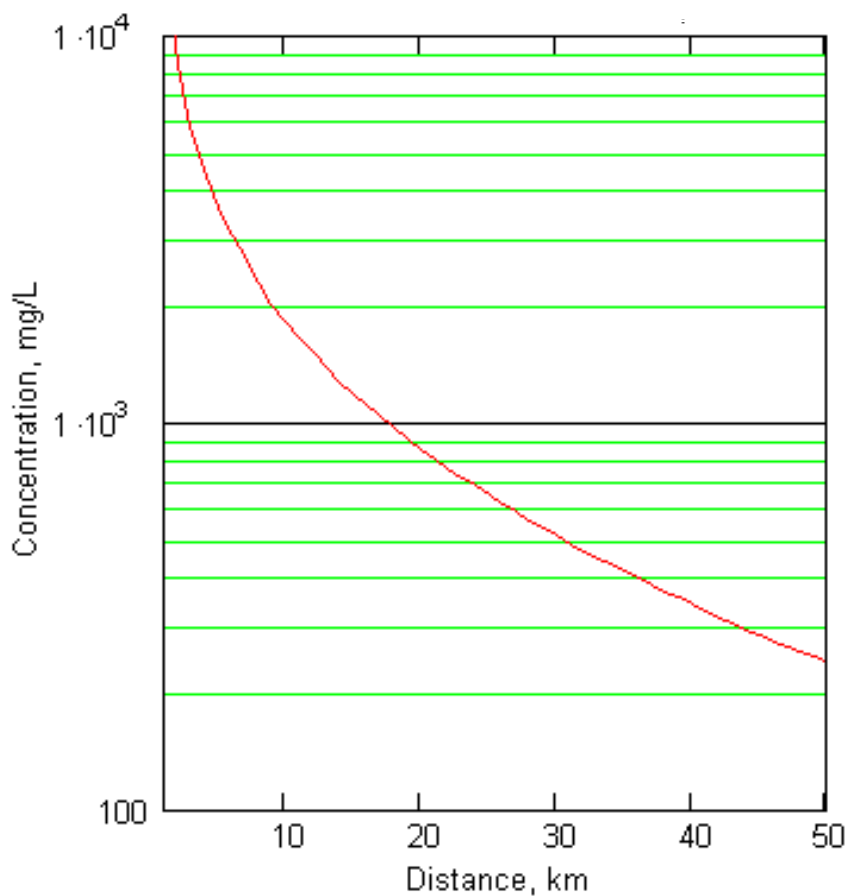
Figure 5-2. Peak concentrations of ethanol in a channel of the Sacramento River above Lake Shasta after a hypothetical tank-car release. Concentrations are based on an estimate of the maximum probable river-flow velocity for peak concentration (see Appendix B) and a biodegradation half-life of 24 h for ethanol (representing k_{tot} in Equation [5-5]).
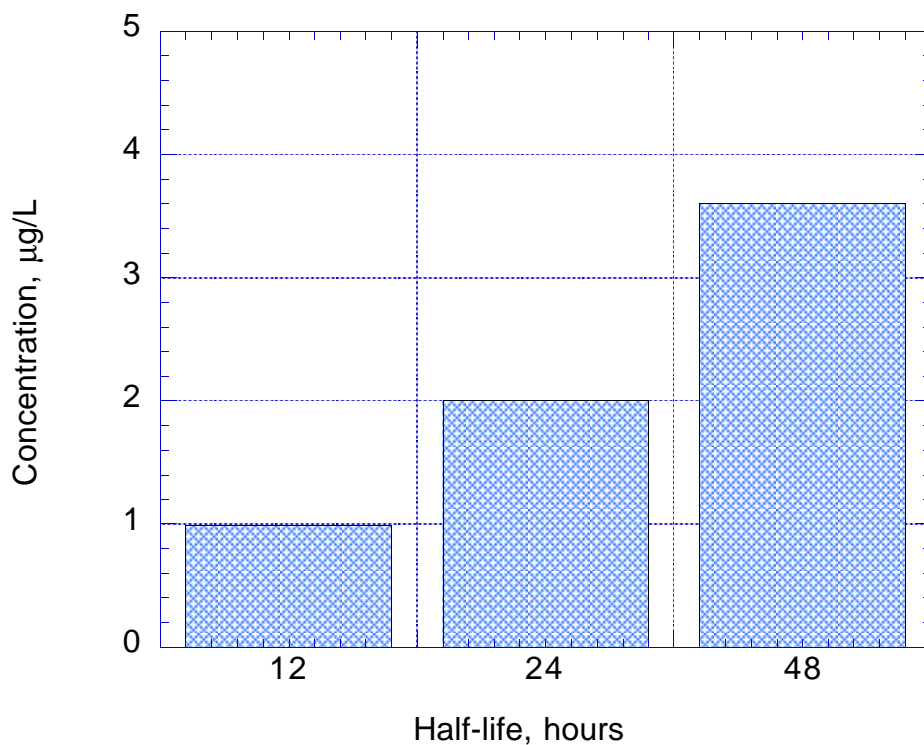
Figure 5-3. Predicted peak concentrations of ethanol in epilimnion waters of Donner Lake after a seven-day period based on alternative biodegradation half-lives and a constant discharge of 40 kg/d from watercraft. Effective depth of the epilimnion for mass transport is 8 m, and the wind velocity is 3 m/s.

Tables

Table 5-1. **Physicochemical properties for MTBE and ethanol.**

Property	Chemical	
	MTBE	**Ethanol**
Molecular weight (g/mol)	88.15	46.07
Density as liquid (g/mL) at 20°C	0.740[a]	0.789[b]
K_{OW} (dimensionless)	8.71[c]	0.50[c]
Vapor pressure (Pa) at 25°C	32,664[d]	7869[e]
Solubility (mol/m^3)	476 (at $\cong$ 20°C)[f]	Miscible in water[g]
Henry's law (Pa-m^3/mol) at 25°C	53.5[h]	0.64[i]
Henry's law (dimensionless = H/RT)	0.0216	0.00026

[a] Reported by MacKay *et al.* (1993) and based on three cited, closely agreeing recent values.

[b] Reported by MacKay *et al.* (1995) and based on four cited, closely agreeing recent values.

[c] Reported by Syracuse Research Corporation (SRC) (1999 WebSite) and based on one cited, recent value, for each substance.

[d] Reported by Budavari *et al.* (1989).

[e] Reported by Boublík *et al.* (1984) and based on one cited value.

[f] Measured value reported by Stephenson (1992).

[g] Reported by Riddick *et al.* (1986).

[h] Reported by Robbins *et al.* (1993) as a measured value obtained using static headspace method.

[i] Reported by Hine and Mookerjee (1975) and based on two cited sources.

Table 5-2. Comparison of the predicted mass loadings, peak concentrations, and loss-rate constants for a MTBE release into Donner Lake[a].

Depth of epilimnion h_{ep}, m	Wind velocity u_a, m/s	Loss-rate constant k_v, 1/d	MTBE mass in epilimnion $M_{s,ep}$, kg	MTBE-peak concentration[b] $C_{s,ep}$, μg/L
7	2	0.041	244	9.7
7	3	0.054	233	9.2
8	2	0.036	248	8.6
8	3	0.048	238	8.3
9	2	0.032	251	7.7
9	3	0.043	242	7.5
10	2	0.029	253	7.0
10	3	0.039	245	6.8

[a] Release rate from watercraft is 40 kg/day for seven days.

[b] The dilution volume is calculated as the product of the depth of the epilimnion and the estimated surface area of the lake (that is, 3.6×10^6 m^2, from McCord and Schladow [1998]). Mass loadings and peak concentrations are for the end of the seven-day period and are calculated from Equations (5-7) and (5-8), respectively.

Appendix A
Estimation of Mass-transfer Parameters

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Estimation of Mass-transfer Parameters

The key parameter in determining the rate constant for volatilization is the mass-transfer velocity, or the rate with which a compound moves from water to air as a function of its physicochemical properties and environmental conditions, such as the water velocity of a stream, water temperature, and wind velocity. The mass-transfer velocity is estimated using a two-layer transfer model in which there are two thin, stagnant films at the air-water exchange boundary—one is a water film and the other a gas film (see Liss and Slater, 1974; Schwarzenbach *et al.*, 1993). Contaminant movement in these layers is via diffusion, whereas turbulent flow in air and water adjacent to these regions is the dominant method of contaminant transport and mixing. The total transport velocity across these layers is calculated as the reciprocal of the sum of the resistances to transport in the water and air phases, or

$$v_{tot} = [r_w + r_a]^{-1}, \tag{A–1}$$

where the water and air-phase resistances are computed from

$$r_w = \frac{1}{v_w} \tag{A–2}$$

$$r_a = \frac{1}{v_a H_L} \tag{A–3}$$

and the transfer velocities for water and air are estimated from

$$v_w = \phi \left(D_{O_2} \frac{u_w}{h_{riv}} \right)^{0.5} 1.0241^{(t-20)} \quad \text{(for rivers, from Pankow } et\ al.,\ 1996), \tag{A–4}$$

$$v_w = \phi \left(4 \times 10^{-4} + 4 \times 10^{-5} u_a^2 \right) \times cf \quad \text{(for lakes, from Schwarzenbach } et\ al.,\ 1993), \tag{A–5}$$

$$v_a = \alpha \left(0.2 u_a + 0.3 \right) \times cf \quad \text{(from Schwarzenbach } et\ al.,\ 1993), \tag{A–6}$$

given

v_{tot}	=	total mass-transfer velocity through the air and water layers, m/d;
r_w	=	resistance to mass transport in air, d/m;
r_a	=	resistance to mass transport in water, d/m;
v_a	=	air-side mass-transfer velocity, m/d;

H_L =   dimensionless Henry's law constant;

υ_w =   water-side mass-transfer velocity, m/d;

D_{O_2} =   diffusivity of oxygen in water, 1.8×10^{-4} in m^2/d at 20 °C;

u_w =   water-current velocity in river or stream, m/d;

ϕ =   compound-specific adjustment factor for the water-side transfer velocity (unitless);

u_a =   wind velocity at a height of 10 m, m/s;

h_{riv} =   depth of river or stream (or h_{ep} for depth of epilimnion of lake), m;

t =   temperature of water, °C;

cf =   conversion factor of 864 m/d per cm/s;

and

α =   compound-specific adjustment factor for the air-side transfer velocity (unitless).

The rate constant for volatilization (k_V) from a river or stream is equal to υ_{tot}/h_{riv} (from Pankow *et al.*, 1996), while for lakes it is equal to υ_{tot}/h_{ep}, where h_{ep} is the depth of the lake's epilimnion (Ulrich *et al.*, 1994). The values of ϕ and α for ethanol and MTBE given in Pankow *et al.* (1996) are 0.738 and 0.753, and 0.586 and 0.558, respectively.

The relative importance of the air- and water-side boundary layers in controlling mass transport can be evaluated by comparing the air and water resistances. According to Schwarzenbach *et al.*, (1993), values of $r_a/r_w > 10$ indicate that mass transfer is controlled by the air film, whereas values below 0.1 indicate that mass transfer is controlled by the water film. Values of r_a/r_w between 0.1 and 10 demarcate a region where both boundary layers influence mass transport. For ethanol, both layers are important, although the air-side resistance is greater than the water-side resistance. The mass transfer for MTBE, in contrast, is controlled primarily by the water-side boundary layer.

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Appendix B
Transport Parameters for Riverine Releases

Appendix B

Transport Parameters for Riverine Releases

A spill of a soluble substance into a river creates a dispersing plume that gradually spreads out in a longitudinal direction as a function of time. Dispersion occurs as the plume moves in a meandering stream channel, encountering various forms of current-induced turbulence. For a conservative contaminant, the mass within the plume remains constant with time, and as the plume spreads out along the direction of transport, the peak concentration decreases with time. Consequently, to estimate the amount of dispersion that has occurred during transport, estimates of the plume's travel time are needed. Travel time is estimated by determining the distance traveled from the release point to the measurement (or receptor) location and the velocity of the peak concentration within the plume.

Jobson (1996) developed a series of empirical formulas for estimating the average velocity of the plume's peak concentration and its maximum probable velocity. Using tracer data from a number of watersheds, the plume velocities are computed from

$$V_{pc} = 0.094 + 0.014\ D_{area}^{0.919}\ Q_{adj}^{-0.469}\ R_{slp}^{0.159}\ \frac{Q}{D_{area}} \qquad \text{(B-1)}$$

$$V_{mpc} = 0.25 + 0.02\ D_{area}^{0.919}\ Q_{adj}^{-0.469}\ R_{slp}^{0.158}\ \frac{Q}{D_{area}} \qquad \text{(B-2)}$$

where

$$D_{area} = W_{area}^{1.25}\ \frac{\sqrt{g}}{Q_{ave}}, \qquad \text{(B-3)}$$

$$Q_{adj} = \frac{Q}{Q_{ave}}, \qquad \text{(B-4)}$$

and

V_{pc} = velocity of the peak concentration in a dispersing plume, m/s;

V_{mpc} = maximum probable velocity of the peak concentration in a dispersing plume, m/s;

W_{area} = watershed-drainage area, m^2;

g = acceleration due to gravity, 9.8 m/s^2;

Q_{ave} = annual-average volumetric-discharge rate of the river at receptor location, m^3/s;

Q = volumetric-discharge rate of the river at the time of the release, m^3/s;

R_{slp} = slope of the river channel, m/m;

D_{area} = dimensionless drainage area; and

Q_{adj} = dimensionless relative discharge.

The dissipation rate constant for the peak concentration in a plume is estimated from

$$k_{pc} = 857 T_{pc}^{-0.760} \left(\frac{Q}{Q_{ave}} \right)^{-0.079}$$ (B-5)

where T_{pc} (in hours) is the arrival time of the peak-concentration (pc) at a receptor location downstream from the release point, which is equal to the downstream distance from the source to receptor divided by the peak-concentration (pc) velocity or maximum probable peak-concentration (mpc) velocity (that is, V_{pc} or V_{mpc}).

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Appendix C
Changes in MTBW and BTEX
Concentrations in Lake Tahoe, CA-NV,
Following Implementation of a Ban on
Selected Two-stroke Marine Engines

Appendix C
Changes in MTBE and BTEX Concentrations in Lake Tahoe, CA-NV, Following Implementation of a Ban on Selected Two-stroke Marine Engines

Brant C. Allen
John E. Reuter

Tahoe Research Group
University of California, Davis
Davis, CA 95616

ABSTRACT

Effective June 1, 1999, the Tahoe Regional Planning Agency imposed a ban on certain types of two-stroke marine-engine technologies. Previous studies had shown that these types of two-stroke carbureted engines accounted for only 11–12% of the total fuel used by watercraft on Lake Tahoe, but they were responsible for approximately 90% of the methyl tertiary butyl ether (MTBE) emissions to the lake. In 1999, Lake Tahoe was monitored in late August and over the Labor Day weekend when peak boating activity traditionally occurs. The purpose of the monitoring was to determine if concentrations of MTBE and gasoline constituents (benzene, toulene, ethyl benzene, and xylene[BTEX]) were affected by implementation of the new marine-engine policy. Samples were taken on three dates: (1) mid-week, (2) after a weekend, and (3) after Labor Day. They were taken from mid-lake (open-water locations), at ten stations located around the perimeter of the lake, and at ten "hot spots" along the south shore where boating and boating-related activities are high. The 1999 results showed a significant decline in both MTBE and BTEX compounds when compared to 1997–1998 levels. Many of the 1999 concentrations of MTBE were below the 0.06-µg/L limit of analytical detection, in contrast to previous monitoring that had many fewer samples this low. High levels of MTBE were still found at certain "hot spots," but these levels were attributed to isolated boating actions not related to overall boating intensity. Combined, the data strongly suggest that the ban on certain types of two-stroke carbureted engines at Lake Tahoe has been very successful in reducing concentrations of both MTBE and BTEX.

INTRODUCTION

Discovery of the fuel oxygenate, methyl tertiary butyl ether (MTBE), in groundwater, lakes, and reservoirs used for drinking water raised considerable concern among health officials and water suppliers. The U.S. Environmental Protection Agency (US EPA) has classified MTBE as a possible human carcinogen. Recent California legislation has established primary and secondary

drinking-water standards at 13 µg/L and 5 µg/L, respectively. In March 1999, the Governor of California called for a statewide phaseout of MTBE as a fuel additive to be completed by the end of 2002.

Since 1997, the Lake Tahoe basin has received considerable state and national attention with regards to MTBE contamination of both groundwater drinking supplies and the lake itself. Contamination of groundwater wells serving the City of South Lake Tahoe is considered to pose more of a potential threat to public health than MTBE concentrations that have been found in the waters of Lake Tahoe. However, because Lake Tahoe has been designated as an Outstanding National Water Resource (ONWR) under the federal Clean Water Act, protection of the lake from controllable sources of pollution is paramount. Samples collected by the Tahoe Research Group (TRG) at the University of California at Davis, the University of Nevada at Reno (UNR), and the U.S. Geological Survey (USGS) during the summers of 1997 and 1998 showed detectable levels of MTBE and the fuel constituents (benzene, toluene, ethyl benzene, and xylenes [BTEX]) lake-wide (Allen *et al.,* 1998). Concentrations were shown to vary with the level of motorized watercraft traffic. However, at specific locations, levels exceeded not only the California drinking-water standards but also the higher US EPA advisory value of 35 µg/L. Samples from open water in the middle of the lake, where little summer boating occurs, revealed the presence of fuel constituents to a depth of 10 m, but at concentrations near or below the analytical levels of detection (mean value for MTBE and BTEX of 0.3 µg/L) (Allen *et al.,* 1998).

Along the shoreline of the lake where motorized watercraft activity is more common, fuel-constituent concentrations were found to be about an order of magnitude higher (for example, 2.6-µg/L mean value for MTBE). However, these shoreline concentrations were still below the established drinking-water standards. In areas where motorized watercraft traffic is considered to be exceptionally high (such as marinas and fueling facilities), mean concentrations for both MTBE and benzene during certain times of the summer boating season exceeded primary drinking-water standards. Further investigation by the California Air Resources Board (CARB) and UNR into the direct contribution of fuel constituents from various engine technologies revealed that carbureted two-stroke engines were contributing a disproportionate share of the fuel-component load to Lake Tahoe (Miller, no date). In fact, Allen *et al.* (1998) calculated that while using only 11 to 12% of the total fuel used for Lake Tahoe boating, these engines contributed 90% of the MTBE to the water. In contrast, four-stroke engines consumed 87% of the fuel but were responsible for only 8% of the estimated MTBE loading to the lake from all marine engines.

Based on the results of these cumulative studies, the Tahoe Regional Planning Agency (TRPA) banned certain types of two-stroke marine-engine technologies (that is, carbureted two-stroke engines). This ban took effect on June 1, 1999. The City of South Lake Tahoe took additional steps to rid the Tahoe basin of MTBE by selling MBTE-free gasoline. Under pressure from the Governor of California, several large oil companies had begun producing gasoline without MTBE and delivering it to the south end of the lake. While this program was intended to reduce the risk of further contamination of groundwater aquifers, it may also have had an effect on concentration of MTBE in the lake. Because fuel costs at marine facilities are significantly higher than at roadside gas stations, conceivably many boaters would choose to refuel while their vessel was still on the trailer.

   With both programs to abate MTBE loading to the lake and groundwater in place by late spring 1999, the summer boating season was expected to produce lower levels of in-lake fuel constituents. We began sampling in August to evaluate the effectiveness of these changes; that is, we compared lake concentrations of MTBE and BTEX in the summer of 1999 to those in the summers of 1997 and 1998.

METHODS

   We focused our sampling on locations which had had positive results (that is, those sites where these constituents had been found during the 1997 and 1998 monitoring). We selected sampling locations in Lake Tahoe that would best reflect any changes in MTBE and BTEX concentrations that may have resulted from policy decisions within the basin. Therefore, we separated site selections into three categories: 1) open-water, offshore areas above a depth of 10 m, 2) near shore, at locations around the perimeter of the lake, where the majority of boat traffic transits the lake, and 3) locations where boat traffic is concentrated ("hot spots"), often associated with launch ramps, refueling facilities, marinas, or a combination of the above (Figure C-1). Within each category, we chose specific sites, whenever possible, to replicate those sampled in previous years.

   The timing of our sampling, in late August and after the Labor Day weekend in September, coincided with the peak of the summer boating season. To avoid potential biases resulting from increased boating on weekends and holidays, we chose three sampling dates. For mid-week days, we chose Wednesday, August 25, and Thursday, August 26, 1999. For weekends, we collected samples from the following Monday (August 30); and for the Labor Day weekend we took samples on the Tuesday after the holiday (September 7).

   At all locations, with the exception of mid-lake, water samples were taken by hand at a depth of 0.5 m. (Our previous sampling at Lake Tahoe showed this to be a representative depth for the near-shore stations.) At each location, we submerged a closed volatile organic analysis (VOA) vial to the sampling depth and then opened it and allowed it to fill completely. We replaced the cap while the vial was still submerged. We checked the samples to ensure no air space remained within the VOA vials before placing them on ice in a cooler. The mid-lake samples were collected using a 1.2-L, stainless-steel Kemmerer well sampler with Teflon end-caps. The sampler was lowered to depth and closed with a messenger. We then transferred the water to a VOA vial and filled it until no air spaces remained. All samples were kept on ice from collection through transport to Lawrence Livermore National Laboratories (LLNL) in Livermore, CA. All analytical determinations were made by LLNL staff at their facilities (Koester, 1999). Analyses were performed using a gas chromatograph/mass spectrometer (GC/MS) operated in the selected-ion monitoring mode and in accordance with US EPA Method 8260. An internal standard of deuterated-MTBE was used to quantify MTBE and also to monitor instrument performance. The limit of quantification obtained by this procedure for MTBE is 0.06 parts per billion (ppb).

RESULTS

   The raw data, as supplied by the LLNL laboratory, are presented in Table C-3. Open lake and near-shore samples showed a significant decrease in MTBE concentration when compared to data collected in 1997 and 1998 (Table C-1). In general, ambient concentrations decreased by an

order of magnitude (a factor of ten). Samples around the north end of the lake (Glenbrook to Homewood) were at or below the 0.06-µg/L level of detection. The samples we collected in the vicinity of the south end of the lake (Zephyr Cove to Emerald Bay) showed a similar drop in concentration from previous years but remained above the level of detection at a few tenths of a part per billion (µg/L).

Ambient concentrations of the BTEX compounds at the near-shore locations were also found to be lower than levels recorded during the past two years of monitoring (Table C-2). However, we were unable to determine changes in ambient concentrations when data from all three years (1997, 1998, and 1999) were below the analytical level of detection, as was the case for BTEX at all samples taken from open water and at the near-shore sites of Glenbrook and Homewood.

To further characterize fuel-constituent concentrations, we collected samples from isolated areas where motorized watercraft traffic is heavy and above the levels observed at the shoreline locations. These "hot spots" are typically associated with marinas, launch ramps, and refueling facilities. While all ten of the selected sites had greater mean fuel-constituent concentrations than the open-shoreline and open-water areas, only four locations approached or exceeded drinking-water standards. The remaining six "hot spots" had fuel-constituent concentrations similar to near-shore areas sampled during the 1997 and 1998 monitoring. At the four "hot spots" where fuel-constituent concentrations neared or exceeded drinking-water standards, MTBE and BTEX concentrations were highly variable. MTBE concentrations ranged from 0.46 µg/L up to 56.5 µg/L. This highend value is over four times the primary drinking-water standard of 13 µg/L. There was no statistically significant difference in concentration for MTBE or any of the BTEX compounds between any of the three years of data at the "hot-spot" locations (Tables C-1, C-2a, and C-2b). The dramatic difference in results between these "hot spots" and the remainder of the lake suggests that source contamination has not been completely eliminated by the regulatory actions taken to date, but that contaminants entering the lake were significantly reduced in the summer of 1999.

DISCUSSION

The sampling dates selected during this study were at the end of the summer boating season during August and after the Labor Day weekend in September. Fuel-constituent concentrations in surface waters can peak following the Fourth of July weekend with changes in concentration being attributed to the dramatic increase in recreational boating (Reuter *et al.,* 1998). However, for a sampling program which more accurately characterizes the summer fuel-constituent load to a waterbody, rather than a worst-case, single-day event, the month of August has proven to be appropriate. Allen *et al.* (1998) showed that mean concentrations of MTBE and BTEX compounds were the highest at Lake Tahoe during August.

With the exception of a few of the "hot spots," the data we collected during this study showed little variation between sampling dates. Both the open-water (mid-lake) and near-shore samples (with the exception of the Edgewood site) remained within a few hundredths of a µg/L at each site over the course of the three days, allowing us to pool the data for comparisons to the monitoring data collected in previous years.

The "hot spots" around the south end of the lake showed greater variation over the three sampling dates. However, concentrations at individual sites did not change consistently between the three sampling dates. Half of the sites recorded their highest concentrations during the mid-

week sampling, which was expected to represent the lowest concentrations due to suspected lower boat traffic. The remainder of the sites recorded their highest values following the Labor Day weekend, which is to be expected due to higher boating activity. The lowest values at each of the "hot spots" occurred on the sampling date following the regular summer weekend. It is assumed that this was a result of a high-wind event on both Sunday and Monday, keeping many boaters on shore and possibly allowing increased volatilization rates of fuel constituents from the water. We also suspect that at the "hot spots," variation in MTBE concentration within a given day was high. For example, if there had been a minor spillage during fueling, or if a boat's bilge water had drained while it was being removed from the lake, concentrations would be expected to be temporarily higher in the vicinity of these activities. It was beyond the scope of this study to determine if the higher concentrations persisted throughout the day or if they were simply associated with a single action as described above.

Comparisons of data collected during this study with that of previous years shows a dramatic decrease in MTBE concentration at both offshore and near-shore locations (86.7% and 95.8%, respectively). This demonstrates that programs to eliminate MTBE from Lake Tahoe are having an effect. The offshore and most of the near-shore locations around the lake had MTBE concentrations at or near the analytical limit of detection (LOD) throughout the sampling period. In fact, if we had used the LOD of 0.1 µg/L from the 1997 and 1998 monitoring, instead of the very low LOD of 0.06 µg/L, samples from all but Emerald Bay, Kiva Beach, and Edgewood would have been below detection. These remaining three locations also had dramatic decreases in 1999, but the level of motorized watercraft traffic in these areas is greater than in other portions of the lake (Nevada Division of Wildlife, 1988) resulting in higher fuel-constituent concentrations. It is important to recognize that none of the recorded concentrations around the near-shore or offshore during 1999 ever approached California or Nevada drinking-water standards.

The sampling of "hot spots" around the south end of Lake Tahoe resulted in highly variable results (that is, an MTBE range <0.06 to 56.5 µg/L). MTBE samples collected at Ski Run Marina exceeded the California primary drinking-water standard of 13 µg/L by four-fold on two separate sampling dates. Additionally, the California drinking-water standard for benzene (0.1 µg/L) was surpassed on the post-Labor Day sampling (September 1999). These samples stand out from the rest as being extremely high even for the "hot spot" locations. The reasons may be due to above-average concentration of boats per unit-area or some problem with operations at the facilities. The two other locations where measured concentrations of MTBE approached or exceeded California drinking-water standards were associated with boat-launch ramps. However, because neither boat-ramp location is in the immediate proximity of fueling facilities, the fuel constituents may have come from the boats themselves.

While it is unclear how the fuel entered the water, any number of human errors and boat malfunctions could have contributed. One distinct possibility associated with launch ramps is the draining of the bilge while removing the boat from the water. Either the intentional removal of boat plugs to allow draining while the boat was on the incline ramp or the automatic operation of electrical bilge pumps when water rushed to the back of the boat causes fuel-laden water to flow directly into the lake in the vicinity of the ramp.

CONCLUSION

Overall, fuel-constituent concentrations in Lake Tahoe in 1999 were down dramatically from previous monitoring years (1997 and 1998), possibly as a result of the TRPA regulation that banned certain types of two-cycle marine-engine technologies, or as a byproduct of some service stations within the Tahoe basin selling MTBE-free fuel.

We compared the decreases in ambient MTBE and toluene concentrations to determine which of the corrective actions was having the greatest impact on Tahoe water quality. If the MTBE-free fuel was having the greatest impact, we expected the ambient MTBE concentrations to decrease while toluene concentrations in the lake would remain near the levels recorded in 1997 and 1998. If the new boating regulations were having the greatest impact, we expected both MTBE and toluene concentrations to drop. Indeed, both mean MTBE and mean toluene concentrations did drop significantly (95.8% and 88.3%, respectively), indicating that the elimination of the highly polluting, carbureted two-stoke engines is having an impact on water quality.

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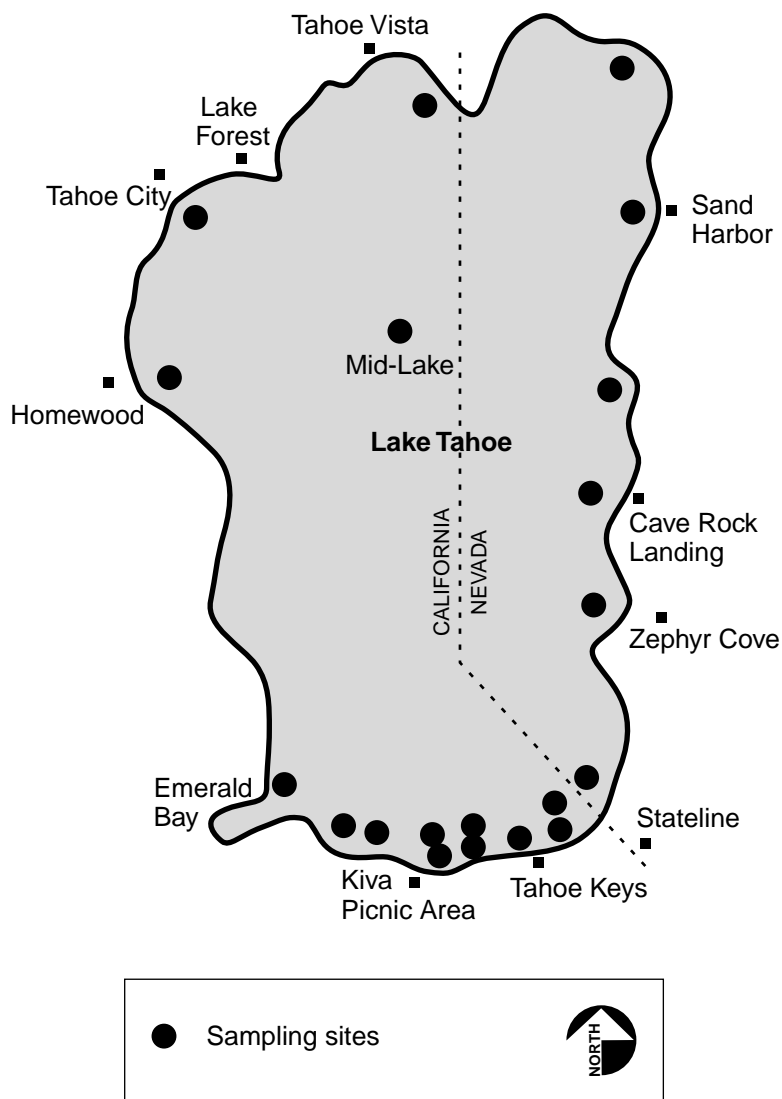
Figure 5-**1.　1999 sampling locations at Lake Tahoe.**

Table C-1. Comparative Lake Tahoe MTBE concentrations, 1997, 1998, 1999[a].

Site	MTBE Concentration (μg/L)		
	1997[b]	1998[c]	1999[d]
Mid-lake	0.54	0.28	0.04
Incline Village	0.45	0.84	0.05
Kings Beach	1.7		0.08
Tahoe City	2.85	1.1	0.04
Homewood	0.45	0.78	0.06
Emerald Bay		4	0.33
Kiva Beach		1.8	0.1
Edgewood		2.4	0.2
Zephyr Cove	1	1.3	0.08
Glenbrook	0.3	0.47	0.03
Sand Harbor			0.06
Cave Rock			0.18
Zephyr Pier			0.15
Ski Run Inside			26.96
Ski Run Outside	20.8		19.77
El Dorado Ramp			2.68
Tahoe Keys Ramp			7.06
Tahoe Keys Channel	0.68	2	1.8
Camp Rich Pier	1.79		0.16
Camp Rich Pumps			0.11
Ski Boat Beach			0.1

[a] When more than one data point exists at a single site within a given year, a mean value is presented ($<0.1 = 0.05$ for calculation of mean).

[b] 1997 data was collected by the University of Nevada at Reno (UNR), and the United States Geological Survey (USGS) during July, August, and September.

[c] 1998 data was collected by USGS and Tahoe Research Group (TRG) in August and September.

[d] 1999 data was collected by TRG during August and September.

Table C-2a. Comparative fuel-constituent data (BTEX), 1997, 1998, and 1999[a].

Site	Benzene concentration, (μg/L)			Toluene concentration (μg/L)		
	1997[b]	1998[c]	1999[d]	1997[b]	1998[c]	1999[d]
Mid-Lake	0.03	0.05	0.05	0.05	0.06	0.04
Incline Village	0.05	0.17	0.16	0.13	1	0.14
Kings Beach	0.13		0.1	0.68		0.18
Tahoe City	0.24	0.28	0.05	1.24	0.64	0.14
Homewood	0.05	0.05	0.05	0.15	0.27	0.06
Emerald Bay		0.44	0.18		1.5	0.24
Kiva Beach		0.17	0.07		0.78	0.16
Edgewood		0.21	0.07		1	0.17
Zephyr Cove	0.15	0.61	0.07	0.7	4.4	0.12
Glenbrook	0.04	0.05	0.05	0.1	0.27	0.08
Sand Harbor			0.05			0.11
Cave Rock			0.12			0.32
Zephyr Pier			0.13			0.14
Ski Run Inside			0.14			0.22
Ski Run Outside	0.88		0.43	7.3		1.75
El Dorado Ramp			0.45			0.92
Tahoe Keys Ramp			0.15			0.28
Tahoe Keys Channel	0.07	0.18	0.31	0.26	0.91	1.53
Camp Rich Pier	0.29		0.17	1.53		0.5
Camp Rich Pumps			0.14			0.38
Ski Boat Beach			0.12			0.33

[a] When more than one data point exists at a single site within a given year, a mean value is presented (<0.1 = 0.05 for calculation of mean).

[b] 1997 data was collected by the University of Nevada at Reno (UNR), and the United States Geological Survey (USGS) during July, August, and September.

[c] 1998 data was collected by USGS and Tahoe Research Group (TRG) in August and September.

[d] 1999 data was collected by TRG during August and September·

Table C-2b. Comparative fuel-constituent data (BTEX), 1997, 1998, and 1999.

Site	Ethylbenzene (µg/L)			m,p, and o Xylene expressed as total xylene (µg/L)		
	1997[b]	1998[c]	1999[d]	1997[b]	1998[c]	1999[d]
Mid-lake	0.02	0.04	0.04	0.04	0.05	0.09
Incline Village	0.02	0.24	0.04	0.1	1.4	0.14
Kings Beach	0.12		0.04	0.72		0.16
Tahoe City	0.24	0.11	0.04	1.39	0.58	0.12
Homewood	0.02	0.04	0.04	0.1	0.26	0.09
Emerald Bay		0.2	0.04		2.1	0.34
Kiva Beach		0.12	0.04		0.81	0.16
Edgewood		0.18	0.04		1.3	0.11
Zephyr Cove	0.12	1.1	0.04	0.75	6.7	0.14
Glenbrook	0.01	0.06	0.04	0.06	0.36	0.13
Sand Harbor			0.04			0.14
Cave Rock			0.09			0.47
Zephyr Pier			0.14			0.83
Ski Run Inside			0.04			0.55
Ski Run Outside	1.1		0.3	6.3		2.34
El Dorado Ramp			1.1			1.29
Tahoe Keys Ramp			0.08			0.47
Tahoe Keys Channel	0.04	0.17	0.12	0.3	1	0.95
Camp Rich Pier	0.4		0.12	1.45		0.84
Camp Rich Pumps			0.19			0.46
Ski Boat Beach			0.08			0.53

[a] When more than one data point exists at a single site within a given year, a mean value is presented (<0.1 = 0.05 for calculation of mean).

[b] 1997 data was collected by the University of Nevada at Reno (UNR), and the United States Geological Survey (USGS) during July, August, and September.

[c] 1998 data was collected by USGS and Tahoe Research Group (TRG) in August and September.

[d] 1999 data was collected by TRG during August and September·

Table C-3. Fuel-constituent concentrations in Lake Tahoe 1999.

MTBE

Offshore	8/25/99	8/30/99	9/7/99	Hot Spots	8/25/99	8/30/99	9/7/99
0m	<.06	<.06	<.06	Cave Rock	0.08	<.06	0.42
3m	<.06	<.06	<.06	Zepher Pier	0.09	0.06	0.31
10m	0.08	<.06	<.06	Ski Run In	1.39	23	56.5
				Ski Run Out	55.6	1.58	2.14
				El Dorado Ramp	4.92	0.46	2.66
Near shore	8/25/99	8/30/99	9/7/99	Tahoe Keys Ramp	7.28	6.93	6.98
Incline Village	0.07		<.06	Tahoe Keys Channel	2.14	0.53	2.72
Kings Beach	0.08		0.07	Camp Rich Pier	0.19	0.08	0.2
Tahoe City	0.07	<.06	<.06	Camp Rich Pumps	0.19	<.06	0.1
Homewood	0.06	0.09	<.06	Ski Boat Beach	0.11	<.06	0.16
Emerald Bay	0.35	0.36	0.29				
Kiva Beach	0.14	<.06	0.13	Blanks	8/25/99	8/30/99	9/7/99
Edgewood	0.14	0.35	0.11	Field	<.06		<.06
Zephyr Cove	0.09	0.06	0.08	mid-lake	<.06		
Glenbrook	<.06		<.06				
Sand Harbor	0.08		<.06				

BENZENE

Offshore	8/25/99	8/30/99	9/7/99	Hot Spots	8/25/99	8/30/99	9/7/99
0m	<0.1	<0.1	<0.1	Cave Rock	<.1	<.1	0.26
3m	<0.1	<0.1	<0.1	Zepher Pier	<.1	<.1	0.28
10m	<0.1	<0.1	<0.1	Ski Run In	<.1	<.1	0.33
				Ski Run Out	<.1	<.1	1.18
				El Dorado Ramp	0.79	<.1	0.51
Near shore	8/25/99	8/30/99	9/7/99	Tahoe Keys Ramp	<.1	<.1	0.36
Incline Village	0.27		<.1	Tahoe Keys Channel	<.1	<.1	0.84
Kings Beach	0.15		<.1	Camp Rich Pier	0.11	<.1	0.34
Tahoe City	<.1	<.1	<.1	Camp Rich Pumps	0.26	<.1	0.11
Homewood	<.1		<.1	Ski Boat Beach	<.1	<.1	0.26
Emerald Bay	0.1	0.19	0.24				
Kiva Beach	<.1	<.1	0.12	Blanks	8/25/99	8/30/99	9/7/99
Edgewood	<.1	<.1	0.12	Field	<0.1		<0.1
Zephyr Cove	0.1	<.1	<.1	mid-lake	0.12		
Glenbrook	<.1		<.1				
Sand Harbor	<.1		<.1				

TOLUENE

Offshore	8/25/99	8/30/99	9/7/99
0m	<.09	<.09	<.09
3m	<.09	<.09	<.09
10m	<.09	<.09	<.09

Near shore	8/25/99	8/30/99	9/7/99
Incline Village	0.11		0.18
Kings Beach	<.09		0.32
Tahoe City	0.18	<.09	0.2
Homewood	<.09	<.09	0.1
Emerald Bay	<.09	0.11	0.57
Kiva Beach	<.09	<.09	0.4
Edgewood	<.09	<.09	0.43
Zephyr Cove	<.09	<.09	0.26
Glenbrook	<.09		0.11
Sand Harbor	<.09		0.18

Hot Spots	8/25/99	8/30/99	9/7/99
Cave Rock	0.13	<.09	0.77
Zepher Pier	<.09	<.09	0.34
Ski Run In	<.09	<.09	
Ski Run Out	<.09	<.09	5.17
El Dorado Ramp	0.24	<.09	2.47
Tahoe Keys Ramp	<.09	<.09	0.76
Tahoe Keys Channel	<.09	<.09	4.5
Camp Rich Pier	<.09	<.09	1.42
Camp Rich Pumps	0.6	0.15	0.4
Ski Boat Beach	<.09	<.09	0.89

Blanks	8/25/99	8/30/99	9/7/99
Field	0.18		<.09
mid-lake	0.27		

ETHYLBENZENE

Offshore	8/25/99	8/30/99	9/7/99
0m	<.09	<.09	<.09
3m	<.09	<.09	<.09
10m	<.09	<.09	<.09

Near shore	8/25/99	8/30/99	9/7/99
Incline Village	<.09		<.09
Kings Beach	<.09		<.09
Tahoe City	<.09	<.09	<.09
Homewood	<.09	<.09	<.09
Emerald Bay	<.09	<.09	<.09
Kiva Beach	<.09	<.09	<.09
Edgewood	<.09	<.09	<.09
Zephyr Cove	<.09	<.09	<.09
Glenbrook	<.09		<.09
Sand Harbor	<.09		<.09

Hot Spots	8/25/99	8/30/99	9/7/99
Cave Rock	<.09	<.09	0.17
Zepher Pier	<.09	<.09	0.34
Ski Run In	<.09	<.09	<.09
Ski Run Out	<.09	<.09	0.82
El Dorado Ramp	2.77	<.09	0.48
Tahoe Keys Ramp	<.09	<.09	0.14
Tahoe Keys Channel	<.09	<.09	0.27
Camp Rich Pier	<.09	<.09	0.27
Camp Rich Pumps	0.47	<.09	<.09
Ski Boat Beach	<.09	<.09	0.15

Blanks	8/25/99	8/30/99	9/7/99
Field	<.09		<.09
mid-lake	<.09		

m,p and o Xylene, expressed as total*

Offshore	8/25/99	8/30/99	9/7/99	Hot Spots	8/25/99	8/30/99	9/7/99
0m	<.18	<.18	<.18	Cave Rock	<.18	<.18	1.23
3m	<.18	<.18	<.18	Zepher Pier	<.18	<.18	2.31
10m	<.18	<.18	<.18	Ski Run In	<.18	<.18	1.48
				Ski Run Out	<.18	<.18	6.83
				El Dorado Ramp	<.83	<.18	3.36
Near shore	8/25/99	8/30/99	9/7/99	Tahoe Keys Ramp	<.18	<.18	1.23
Incline Village	<.24		<.30	Tahoe Keys Channel	<.18	<.18	2.67
Kings Beach	<.19		<.46	Camp Rich Pier	<.18	<.18	2.33
Tahoe City	<.18	<.18	<.33	Camp Rich Pumps	0.57	<.32	0.64
Homewood	<.18	<.18	<.18	Ski Boat Beach	<.18	<.18	1.4
Emerald Bay	<.18	<.26	0.79				
Kiva Beach	<.18	<.18	<.60	Blanks	8/25/99	8/30/99	9/7/99
Edgewood	<.18	<.18	<.30	Field	<.18		<.18
Zephyr Cove	<.18	<.18	<.46	mid-lake	<.18		
Glenbrook	<.18		<.33				
Sand Harbor	<.18		<.36				

*m,p and o xylenes were added for total xylenes.
When either m,p or o xylenes were reported as '<' the total xylenes were also expressed as '<'

m,p-Xylene

Offshore	8/25/99	8/30/99	9/7/99	Hot Spots	8/25/99	8/30/99	9/7/99
0m	<.1	<.1	<.1	Cave Rock	<.1	<.1	1.05
3m	<.1	<.1	<.1	Zepher Pier	<.1	<.1	2
10m	<.1	<.1	<.1	Ski Run In	<.1	<.1	1.22
				Ski Run Out	<.1	<.1	5.89
				El Dorado Ramp	<.1	<.1	2.83
Near shore	8/25/99	8/30/99	9/7/99	Tahoe Keys Ramp	<.1	<.1	1.04
Incline Village	<.1		0.22	Tahoe Keys Channel	<.1	<.1	2.13
Kings Beach	<.1		0.38	Camp Rich Pier	<.1	<.1	2.03
Tahoe City	<.1	<.1	0.25	Camp Rich Pumps	0.42	0.24	0.56
Homewood	<.1	<.1	0.1	Ski Boat Beach	<.1	<.1	1.21
Emerald Bay	<.1	0.18	0.69				
Kiva Beach	<.1	<.1	0.52	Blanks	8/25/99	8/30/99	9/7/99
Edgewood	<.1	<.1	0.22	Field	<.1		<.1
Zephyr Cove	<.1	<.1	0.38	mid-lake	<.1		
Glenbrook	<.1		0.25				
Sand Harbor	<.1		0.28				

o-Xylene

Offshore	8/25/99	8/30/99	9/7/99
0m	<.08	<.08	<.08
3m	<.08	<.08	<.08
10m	<.08	<.08	<.08

Near shore	8/25/99	8/30/99	9/7/99
Incline Village	0.14		<.08
Kings Beach	0.09		<.08
Tahoe City	<.08	<.08	<.08
Homewood	<.08	<.08	<.08
Emerald Bay	<.08	<.08	0.1
Kiva Beach	<.08	<.08	<.08
Edgewood	<.08	<.08	<.08
Zephyr Cove	<.08	<.08	<.08
Glenbrook	<.08		<.08
Sand Harbor	<.08		<.08

Hot Spots	8/25/99	8/30/99	9/7/99
Cave Rock	<.08	<.08	0.18
Zepher Pier	<.08	<.08	0.31
Ski Run In	<.08	<.08	0.26
Ski Run Out	<.08	<.08	0.94
El Dorado Ramp	0.73	<.08	0.53
Tahoe Keys Ramp	<.08	<.08	0.19
Tahoe Keys Channel	<.08	<.08	0.54
Camp Rich Pier	<.08	<.08	0.3
Camp Rich Pumps	0.15	<.08	0.08
Ski Boat Beach	<.08	<.08	0.19

Blanks	8/25/99	8/30/99	9/7/99
Field	<.08		<.08
mid-lake	<.08		